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| <p>(54) Title: <b>NOVEL ETHYLENICALLY UNSATURATED AMINE SALTS OF SULFONIC, PHOSPHORIC AND CARBOXYLIC ACIDS</b></p> <p>(57) Abstract</p> <p>Disclosed are ethylenically unsaturated amine salts of sulfonic, phosphoric and carboxylic acids. The salts are surface active agents which are especially useful in emulsion polymerization reactions.</p>   |  |   |  |

## NOVEL ETHYLENICALLY UNSATURATED AMINE SALTS OF SULFONIC, PHOSPHORIC AND CARBOXYLIC ACIDS

### BACKGROUND OF THE INVENTION

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#### Field of the Invention:

The present invention relates to novel ethylenically unsaturated amine salts of sulfonic, phosphoric and carboxylic acids. More specifically, the invention relates to ethylenically unsaturated amine salts of alkylbenzene sulfonic acids, alkyl olefin sulfonic acids, alkyl alcohol sulfuric acid esters and alkoxylated alkyl alcohol sulfuric acid esters, and 10 mixtures thereof. Additionally, the invention relates to ethylenically unsaturated amine salts of alkyl carboxylic acids and alkyl phosphoric acids. The salts are polymerizable, surface active agents which are useful in a variety of applications, especially in detergent formulations and in emulsion polymerization processes.

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#### Description of the Related Art

A variety of surface active agents are known to the art, including, for example, anionic, nonionic, amphoteric, and/or cationic surfactants. Anionic surfactants are typically in the form of alkali metal (lithium, sodium, potassium), alkaline earth (calcium, magnesium), ammonium and/or alkanolamine salts of the corresponding anionic acid.

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Surface active agents are useful in a variety of applications, e.g., emulsion polymerization reactions. For example, in a conventional emulsion polymerization of ethylenically unsaturated monomers, one or more surfactants are used to emulsify the monomers and the resulting polymer products, i.e., latexes. The monomers used in emulsion polymerization reactions are generally water-insoluble, but may also be water-soluble. 25 During the polymerization, small portions of monomer are suspended in a continuous aqueous phase. Typically, a water soluble surfactant is present within the aqueous phase to aid in the

suspension of the monomer, with subsequent polymerization via a free-radical polymerization. The water soluble surface active agents, i.e., surfactants, utilized in emulsion polymerization reactions are typically anionic, nonionic, cationic, or zwitterionic surfactants or mixtures thereof.

5        In a traditional emulsion polymerization reaction, discrete, solid polymeric particles are formed during the course of the reaction to form a polymer product latex. Typically, the surfactant employed in such a traditional emulsion polymerization reaction does not react with, i.e., become chemically bonded via carbon-carbon bond formation to, the discrete polymeric particles. Rather, the surfactant remains unreacted in the polymer product latex  
10      after the emulsion polymerization reaction is complete. The unreacted surfactant can interfere with the performance of such polymerization products in coating, adhesive, sealant and elastomer (CASE) applications. The unreacted surfactant may, for example, cause peeling of a latex paint coating, and decreased moisture resistance and scrub resistance in various CASE applications. Additionally, residual surfactant can cause an undesirable "blooming" that leads  
15      to surface irregularities in a resulting CASE that is applied to a substrate.

Several proposals have been made in the prior art to employ a polymerizable surfactant as the surface active agent during an emulsion polymerization reaction. U.S. Pat. No. 5,478,883 (incorporated herein by reference) describes the use of ethylenically unsaturated polymerizable water-soluble nonionic surfactants formed by the reaction of a  
20      diallylamine compound with ethylene oxide, propylene oxide or butylene oxide, in emulsion polymerization reactions. Similarly, U.S. Pat. No. 5,162,475 (incorporated herein by reference) provides alpha-beta ethylenically unsaturated poly(alkylenoxy) polymerizable surface active compounds for use in emulsion polymerization. For additional examples of polymerizable surfactants for use in emulsion polymerization processes, see U.S. Pat. Nos.  
25      4,377,185 and 4,049,608.

### SUMMARY OF THE INVENTION

The present invention provides ethylenically unsaturated amine salts of sulfonic, phosphoric or carboxylic acids, or mixtures thereof. The amine salts of the present invention are polymerizable, surface active agents suitable for use as primary or secondary surfactants  
5 in emulsion polymerization reactions.

The surface active agents of the present invention are especially useful in emulsion polymerization reactions and are generally capable of polymerizing with themselves and/or co-polymerizing with other ethylenically unsaturated monomers of the type which are commonly employed in emulsion polymerization reactions.

10 The surface active agents of the present invention are prepared from readily available, economical raw materials, and generally, their preparation does not require any special handling or equipment. The polymerizable surface active agents may be prepared in a batch mode or a continuous mode; they may be prepared by contacting the ethylenically unsaturated amine with the acid or contacting the acid with the ethylenically unsaturated amine. By  
15 contacting it is meant that the acid(s) is added to the ethylenically unsaturated amine(s) and the components are mixed, or the ethylenically unsaturated amine(s) is added to the acid(s) and the components are mixed. Typically, upon mixing, the acid and the base combine to form an amine salt. As known by one skilled in the art, upon mixing the acid and nitrogenous base together, the nitrogenous base becomes a conjugate acid and the acid  
20 becomes a conjugate base.

The polymerizable surface active agents may alternatively be prepared by contacting the ethylenically unsaturated amine with an alkaline earth or ammonium salt of the acid (e.g., the sodium, potassium, magnesium, calcium, ammonium, or ethoxylated ammonium salts of the acid), whereby the polymerizable surface active agent is formed in situ.

The surface active agents and blends of surface active agents may be prepared in a variety of forms, including but not limited to, liquids, solutions, solids, powders, flakes, semi-solids, gels, "ringing" gels, G-phase liquids, hexagonal phase solids, or thick pastes. The surface active agents may be spray dried, flaked, extruded, and the like. Although not critical

5 to the present invention, the polymerizable, surface active agents may be prepared "neat" or in a conventional solvent such as water, low molecular weight alcohol or hydrocarbon, or a mixture thereof, to produce a solution of the surface active agent. The present invention encompasses surface active agents as salts in dry form and as aqueous solutions. Salts of the surface active agents may be isolated by drying a solution of the surface active agents; a

10 solution of surface active agents may be prepared by dissolving the salt of the surface active agent in water, low molecular weight alcohol or hydrocarbon, or a mixture thereof.

Individual surface active agents of the present invention may be prepared and mixed together to produce a surface active mixture comprising "neat" surface active agents or an aqueous surfactant blend. Additionally, neat or aqueous blends of the surface active agents

15 may be prepared by contacting a blend of two or more ethylenically unsaturated amines with one acid, or by contacting a blend of two or more ethylenically unsaturated amines with a blend of 2 or more acids. Conversely, blends of the surface active agents may be prepared by contacting a blend of two or more acids with one ethylenically unsaturated amine, or by contacting a blend of two or more acids with a blend of two or more ethylenically unsaturated

20 amines.

These and other advantages of the present invention will be apparent from the following description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention encompasses polymerizable, surface active agents which are amine salts comprising:

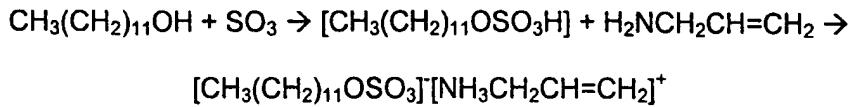
- a) at least one acid, wherein the acid is a sulfonic acid, a carboxylic acid, or a phosphoric acid, or mixtures thereof; and
- 5 b) at least one nitrogenous base, wherein the nitrogenous base contains at least one nitrogen atom and at least one ethylenically unsaturated moiety.

The acids useful in the present invention are generally sulfonic acids, polysulfonic acids, sulfonic acids of oils, paraffin sulfonic acids, lignin sulfonic acids, petroleum sulfonic acids, olefin sulfonic acids, hydroxyolefin sulfonic acids, polyolefin sulfonic acids, polyhydroxy polyolefin sulfonic acids, carboxylic acids, perfluorinated carboxylic acids, carboxylic acid sulfonates, alkoxylated carboxylic acid sulfonic acids, polycarboxylic acids, polycarboxylic acid polysulfonic acids, alkoxylated polycarboxylic acid polysulfonic acids, phosphoric acids, alkoxylated phosphoric acids, polyphosphoric acids, and alkoxylated 15 polyphosphoric acids, fluorinated phosphoric acids, phosphoric acid esters of oils, phosphinic acids, alkylphosphinic acids, aminophosphinic acids, polyphosphinic acids, vinyl phosphinic acids, phosphonic acids, polyphosphonic acids, phosphonic acid alkyl esters,  $\alpha$ -phosphono fatty acids, organoamine polymethylphosphonic acids, organoamino dialkylene phosphonic acids, alkanolamine phosphonic acids, trialkylidene phosphonic acids, acylamidomethane 20 phosphonic acids, alkyliminodimethylene diphosphonic acids, polymethylene-bis(nitrilo dimethylene)tetraphosphonic acids, alkyl bis(phosphonoalkylidene) amine oxide acids, esters of substituted aminomethylphosphonic acids, phosphonamidic acids, acylated amino acids (e.g., amino acids reacted with alkyl acyl chlorides, alkyl esters or carboxylic acids to produce N-acylamino acids), N-alkyl acylamino acids, and acylated protein hydrolysates, and mixtures 25 thereof.

Other acids which are useful in the present invention are selected from the group comprising linear or branched alkylbenzene sulfonic acids, alkyl sulfuric acid esters, alkoxylated alkyl sulfuric acid esters,  $\alpha$ -sulfonated alkyl ester acids,  $\alpha$ -sulfonated ester diacids, alkoxylated  $\alpha$ -sulfonated alkyl ester acids,  $\alpha$ -sulfonated dialkyl diester acids, di- $\alpha$ -sulfonated dialkyl diester acids,  $\alpha$ -sulfonated alkyl acetate acids, primary and secondary alkyl sulfonic acids, perfluorinated alkyl sulfonic acids, sulfosuccinic mono- and diester acids, polysulfosuccinic polyester acids, sulfoitaconic diester acids, sulfosuccinamic acids, sulfosuccinic amide acids, sulfosuccinic imide acids, phthalic acids, sulfophthalic acids, sulfoisophthalic acids, phthalamic acids, sulfophthalamic diacids, alkyl ketone sulfonic acids, hydroxyalkane-1-sulfonic acids, lactone sulfonic acids, sulfonic acid amides, sulfonic acid diamides, alkyl phenol sulfuric acid esters, alkoxylated alkyl phenol sulfuric acid esters, alkylated cycloalkyl sulfuric acid esters, alkoxylated alkylated cycloalkyl sulfuric acid esters, dendritic polysulfonic acids, dendritic polycarboxylic acids, dendritic polyphosphoric acids, sarcosinic acids, isethionic acids, and tauric acids, tall oil fatty acids, and mixtures thereof.

Additionally in accordance with the present invention, suitable acids of the present invention include fluorinated carboxylic acids, fluorinated sulfonic acids, fluorinated sulfonic ester acids, fluorinated phosphonic and phosphinic acids, phosphenic acids, and mixtures thereof.

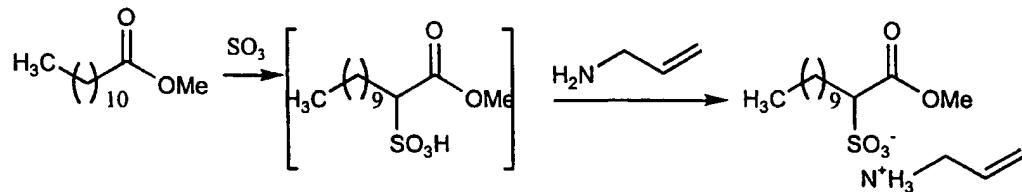
Due to their inherent hydrolytic instability, the sulfuric acid esters are preferably immediately converted to ethylenically unsaturated amine salts. For example, linear dodecyl alcohol is sulfated with  $\text{SO}_3$  to produce an intermediate, hydrolytically unstable, dodecyl alcohol sulfuric acid ester as shown in Scheme I below. The intermediate acid is neutralized with an ethylenically unsaturated nitrogenous base, such as allyl amine, to produce a dodecyl sulfate ethylenically unsaturated amine salt.

Scheme I: Formation of Dodecyl Sulfate Ethylenically Unsaturated Amine Salt

5        Additionally, for example, methyl laurate is sulfonated with  $\text{SO}_3$  to produce an intermediate  $\alpha$ -sulfonated lauryl methyl ester acid, as shown in Scheme II below. This acid is neutralized with an ethylenically unsaturated nitrogenous base, such as allyl amine, to produce an  $\alpha$ -sulfonated lauryl methyl ester ethylenically unsaturated amine salt. Additionally, an  $\alpha$ -sulfonated lauryl methyl ester ethylenically unsaturated amine di-salt may

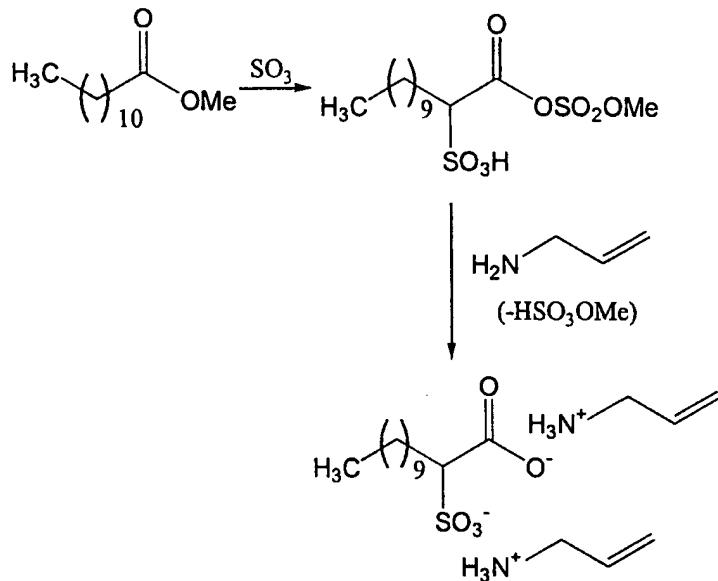
10      be produced as shown below in Scheme III. The  $\alpha$ -sulfonated lauryl methyl ester ethylenically unsaturated amine salt and the  $\alpha$ -sulfonated lauryl fatty acid ethylenically unsaturated amine di-salt may be formed as a mixture depending on the sulfonation conditions employed. The ratio of unsaturated amine salt to unsaturated amine di-salt is readily controlled by sulfonation conditions, well known to those skilled in the art.

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Scheme II: Formation of  $\alpha$ -Sulfonated Lauryl Methyl Ester Ethylenically Unsaturated Amine Salt

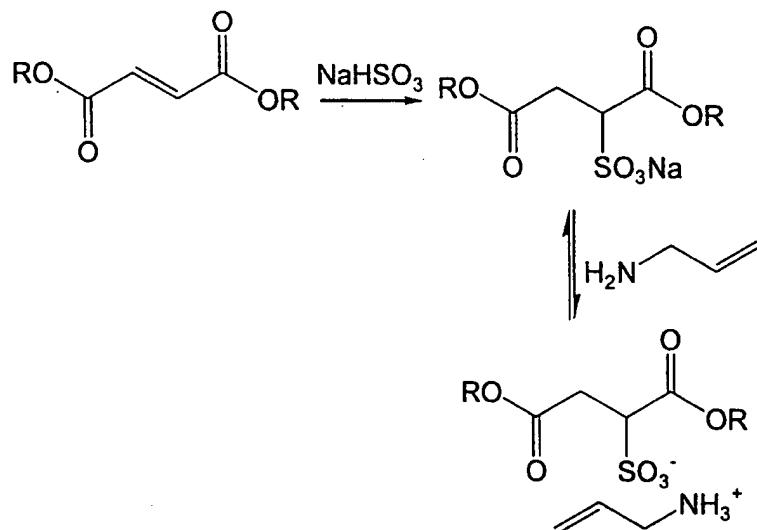
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Scheme III: Formation of  $\alpha$ -Sulfonated Lauryl Methyl Ester Ethylenically Unsaturated Amine Di-Salt



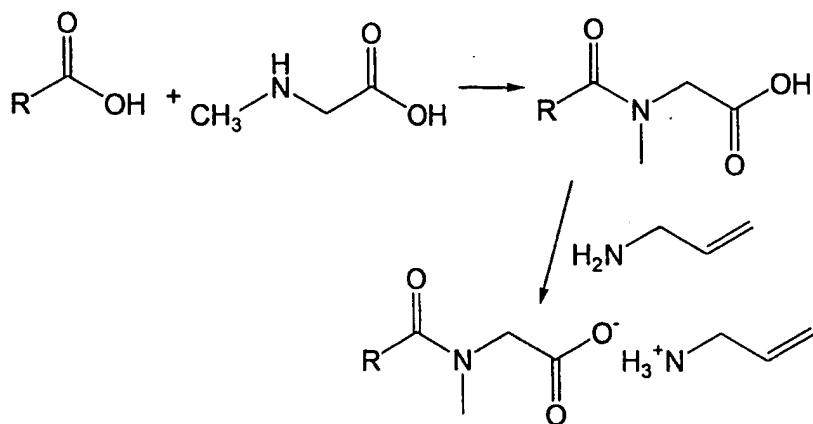
Ethylenically unsaturated amine salts of sulfosuccinate ester acids are typically produced by sulfitation of a succinic acid alkyl diester with sodium bisulfite, followed by 5 ionic exchange with an ethylenically unsaturated nitrogenous base, such as allyl amine, as shown in Scheme IV below.

Scheme IV: Formation of a Sulfosuccinate Ester Ethylenically Unsaturated Amine Salt



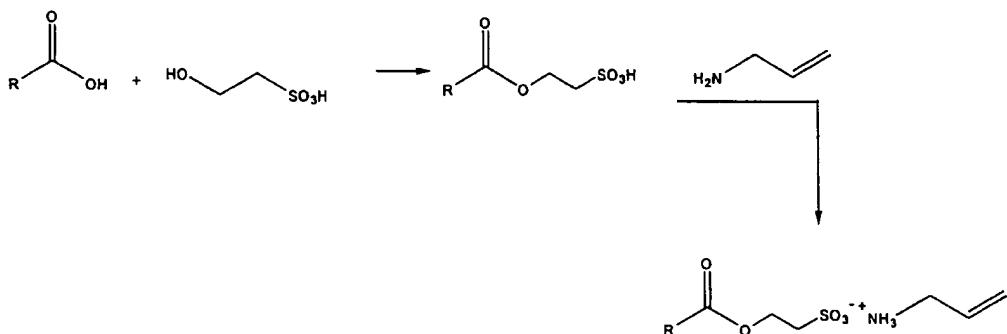
The sarcosinic acid ethylenically unsaturated amine salts are prepared by the amidation of a fatty acid, a fatty acid alkyl ester or a fatty acid chloride with sarcosine, followed by addition of an ethylenically unsaturated nitrogenous base, such as allyl amine, as 5 shown in Scheme V below. Optionally, and somewhat less preferably, the ethylenically unsaturated nitrogenous base is combined with sarcosine to produce the corresponding sarcosine salt, which is then be used to amidate the fatty acid, fatty acid alkyl ester or fatty acid chloride.

10      Scheme V: Formation Of A Fatty Sarcosinate Acid Ethylenically Unsaturated Amine Salt



The isethionic acid ethylenically unsaturated amine salts may be prepared by the esterification of a fatty acid, a fatty acid alkyl ester or a fatty acid chloride with isethionic acid, followed by addition of an ethylenically unsaturated nitrogenous base, such as allyl amine, as shown in Scheme VI below. Additionally, isethionic acid ethylenically unsaturated amine salts may be prepared by esterifying a fatty acid, a fatty acid alkyl ester or a fatty acid chloride with the sodium salt of isethionic acid, followed by ion exchange with an ethylenically unsaturated nitrogenous base, such as allyl amine. Optionally, isethionic acid, or its sodium salt, may be combined with the ethylenically unsaturated nitrogenous base, such as allyl amine, to produce the isethionic acid allyl amine salt, which may then be esterified with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

Scheme VI: Formation Of A Isethionic Acid Ethylenically Unsaturated Amine Salt

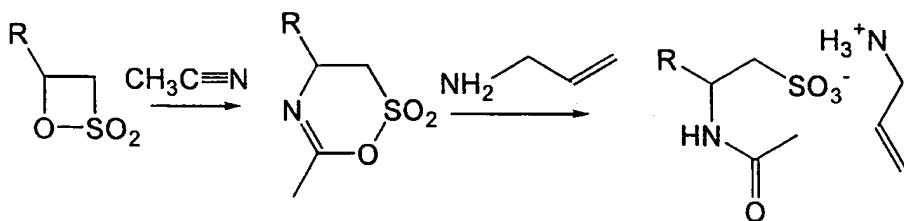


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The preferred acids of the present invention are branched or linear alkylbenzene sulfonic acids, alkyl sulfuric acid esters, alkoxylated alkyl sulfuric acid esters,  $\alpha$ -sulfonated alkyl ester acids, fatty carboxylic acids and phosphoric acid esters, and mixtures thereof. The most preferred acids of the present invention are branched or linear alkylbenzene sulfonic acids, alkyl sulfuric acid esters, and alkoxylated alkyl sulfuric acid esters, and mixtures thereof.

Other objects of the present invention are sulfonic acid salts of ethylenically unsaturated amines, derived from sultone precursors, such as cyclic alkyl sultones. Examples of these sultone-derived sulfonic acid salts (e.g., allyl amine salts) include 2-acetamidoalkyl-1-sulfonates and amino carboxy acid alkyl sulfonates, as shown in Scheme VII and Scheme VIII below.

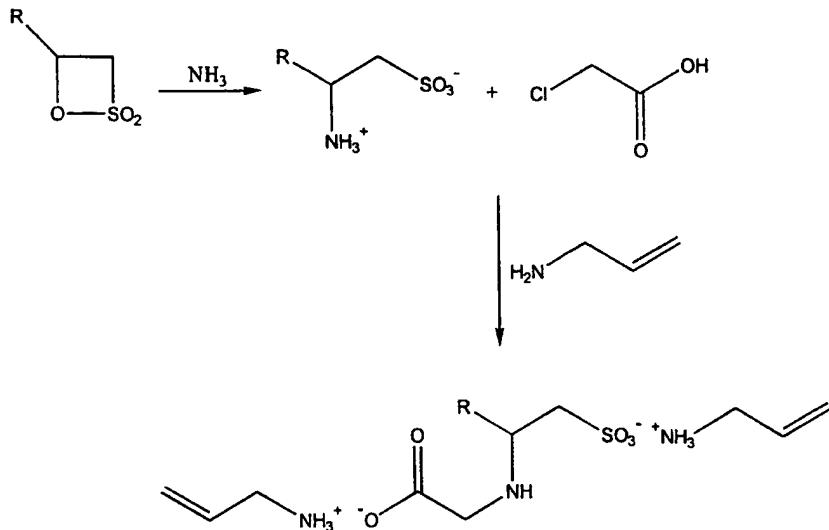
Scheme VII: 2-Acetamidoalkyl-1-Sulfonic Acid Allyl Amine Salts



where R is C<sub>4-24</sub> alkyl.

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Scheme VIII: Amino Carboxy Acid Alkyl Sulfonic Acid Allyl Amine Salts



where R is C<sub>4-24</sub> alkyl.

In general, nitrogenous bases which are useful in the present invention are any  
15 nitrogenous base which contains an ethylenically unsaturated moiety, including various vinyl

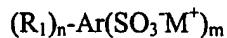
amines. In addition to allyl amine, as shown in the above schemes, other examples of nitrogenous bases that are useful in the present invention are ethylenically unsaturated amines selected from the group comprising vinyl amine, N,N-dimethyl-N-allyl amine, N-methyl N-allyl amine, C<sub>1</sub>-C<sub>24</sub> alkyl allyl amine, C<sub>1</sub>-C<sub>24</sub> alkyl ethoxylated and/or propoxylated allyl amine, C<sub>1</sub>-C<sub>24</sub> dialkyl allyl amine, ethoxylated and/or propoxylated allyl amine diallyl amine, C<sub>1</sub>-C<sub>24</sub> alkyl diallyl amine, ethoxylated and/or propoxylated diallyl amine, triallyl amine, 1,2-diaminoethene, aminocrotonitrile, diaminomaleonitrile, N-allyl-N-cyclopentylamine, N-allylaniline, N-allyl-N-cyclohexylamine, [1-(2-allylphenoxy)-3-(isopropylamino)-2-propanol], 3-amino-2-butenethioamide, bis[4-(dimethylamino)-benzylidene]acetone, 1,4-butanediol bis(3-aminocrotonate), 3-amino-1-propanol vinyl ether, 2-(diethylamino)ethanol vinyl ether, 4-(diethylamino)cinnamaldehyde, 4-(diethylamino)cinnamomitrile, 2-(diethylamino)ethyl methacrylate, diethyl (6-methyl-2-pyridylaminomethylene)maleate, 3-(dimethylamino)acrolein, 2-(dimethylamino)ethyl methacrylate, 4-dimethylaminocinnamaldehyde, 2-(dimethylamino)ethyl acrylate, 3-(dimethylamino)-2-methyl-2-propenal, 9-vinylcarbazole, N-vinylcaprolactam, 1-vinylimidazole, 2-vinylpyridine, 4-vinylpyridine, allyl(diisopropylamino)dimethylsilane, 1-allylimidazole, 1-vinyl-2-pyrrolidinone, N-[3-(dimethylamino)propyl]methacrylamide, 4-[4-(dimethylamino)styryl]pyridine, 2-[4-(dimethylamino)styryl]pyridine, 2-[4-(1,2-diphenyl-1-butenyl)phenoxy]-N,N-dimethylethylamine, 2-[4-dimethylamino)styryl]-benzothiozole, 5-[4-(dimethylamino)phenyl]-2,4-pentandienal, (dimethylamino-methylene)-malononitrile, 4-dimethylaminocinnamomitrile, 4-(dimethylamino)chalcone, [6-(3,3-dimethylallylamino-purine riboside, 3,7-dimethyl-2,6-octadien-1-ylamine, 2-isopropenylaniline, isopropyl 3-aminocrotonate, S-{2-[3-(hexyloxy)benzoyl]-vinyl}glutathione, methyl 3-aminocrotonate, N-methylallylamine, N-methyl-1-(methylthio)-2-nitroetheneamine, oleylamine, tetrakis(dimethylamino)ethylene, 5-[(6,7,8-trimethoxy-4-quinazolinyl)amino]-1-pentanol

nitrate ester, tris(2-methylallyl)amine, N,N,N',N'-tetramethyl-2-butene-1,4-diamine, S-[2-[3-(octyloxy)benzoyl]vinyl]-glutathione, 4,4'-vinylidene-(N,N-dimethylaniline), 2',5'-dimethoxy-4-stilbenamine, 3-(dimethylamino)propyl acrylate, 3-dimethylaminoacrylonitrile, 4-(dimethylamino)-cinnamic acid, 2-amino-1-propene-1,1,3-tricarbonitrile, 2-amino-4-pentenoic acid, N, N'-diethyl-2-butene-1,4-diamine, 10,11-dihydro-N,N-dimethyl-5-methylene-5H-dibenzo[a,d]-cycloheptene-10-ethanamine maleate, 4-(dicyanomethylene)-2-methyl-6-(4-dimethyl-aminostyryl)-4H-pyran, N-ethyl-2-methylallylamine, ethyl 3-aminocrotonate, ethyl- $\alpha$ -cyano-3-indoleacrylate, ethyl-3-amino-4,4-dicyano-3-butenoate, 1,3-divinyl-1,1,3,3-tetramethyldisilazane, N-(4,5-dihydro-5-oxo-1-phenyl-1H-pyrazol-3-yl)-9-octadecen-amide, and N-oleoyl-tryptophan ethyl ester, and mixtures thereof.

More preferred nitrogenous bases of the present invention are allyl amine, diallyl amine, triallyl amine, N-methyl-N-allyl amine, N-allyl N,N-dimethyl amine, methyl 3-amino crotonate, 3-amino crotononitrile, 3-amino-1-propanol vinyl ether, N-methyl N-allyl amine, 2-(dimethylamino)ethyl acrylate, or 1,4-diamino-2-butene, and mixtures thereof. The most preferred nitrogenous bases of the present invention are allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, and 2-(dimethylamino)ethyl acrylate, and mixtures thereof.

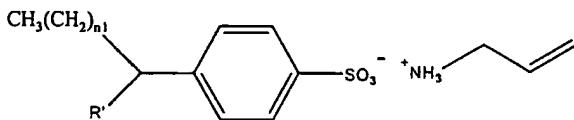
In the methods and compositions of the invention, amine salts are generally preferred over quaternary ammonium compounds.

Accordingly, the present invention encompasses surface active agents of the formula:



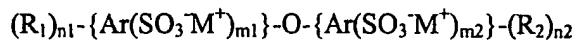
wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1-24 carbon atoms; wherein Ar is a phenyl, polyphenyl, napthyl, polynapthyl, styryl, or polystyryl group, or a mixture thereof; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; wherein n = 1-5 and m = 1-8; and wherein the total number of carbon atoms represented by (R<sub>1</sub>)<sub>n</sub> is at least 5.

In a preferred embodiment R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms, Ar is a phenyl, M<sup>+</sup> is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine or 2-(dimethylamino)ethyl acrylate, and mixtures thereof and n = 1 and m = 1. In another preferred embodiment, the surface active agent is of the formula:



wherein n1 = 4 -18; and wherein R' is hydrogen or saturated or unsaturated hydrocarbon group having from about 1-8 carbon atoms.

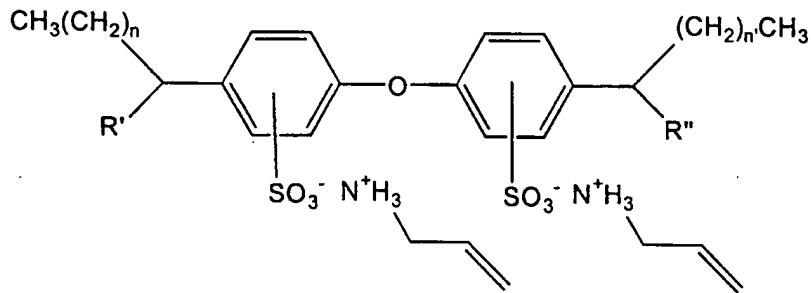
The present invention further encompasses surface active agents of the formula



wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, or saturated or unsaturated hydrocarbon groups having from about 1-24 carbon atoms; wherein Ar is a phenyl, polyphenyl, napthyl, polynapthyl, styryl, or polystyryl group, or a mixture thereof; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; wherein n1 and n2 are independently 0 - 5, provided that n1 and n2 are not both equal to zero; and wherein m1 and m2 are independently 0-8, provided that m1 and m2 are not both equal to zero. In a preferred embodiment, R<sub>1</sub> is hydrogen and R<sub>2</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms, Ar is phenyl, M<sup>+</sup> is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine or 2-(dimethylamino)ethyl acrylate, and mixtures thereof, n1 = 4, n2 = 1, and m1 and m2 both equal one. In another preferred embodiment, R<sub>1</sub> and R<sub>2</sub> are independently saturated or unsaturated hydrocarbon groups having from about 6-24 carbon atoms, Ar is

phenyl,  $M^+$  is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof, n1 and n2 both equal one, and m1 and m2 both equal one. In another preferred embodiment, the surface active agent is of the formula:

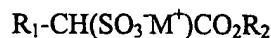
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wherein n and n' are independently 4-18; and wherein R' and R'' are independently hydrogen, methyl, ethyl or propyl.

The present invention further encompasses surface active agents of the formula:

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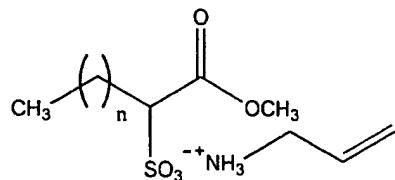


wherein R<sub>1</sub> and R<sub>2</sub> are independently saturated or unsaturated hydrocarbon groups having from about 1- 24 carbon atoms; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base.

In a preferred embodiment, R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms, R<sub>2</sub> is methyl, ethyl, or propyl, or a mixture thereof, and M<sup>+</sup> is a

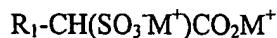
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conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof. In another preferred embodiment, the surface active agent is of the formula:

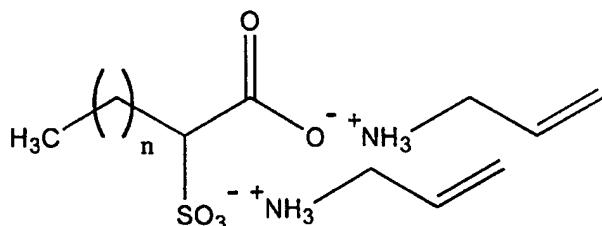


wherein n = 3 - 18.

The present invention further encompasses surface active agents of the formula:



- 5 wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 3 - 24 carbon atoms; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base. In a preferred embodiment, R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms, M<sup>+</sup> is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-10 methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof. In another preferred embodiment, the surface active agent is of the formula:



wherein n = 3 - 18.

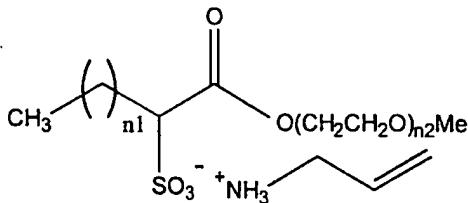
The present invention further encompasses surface active agents of the formula:



- wherein R<sub>1</sub> and R<sub>2</sub> are independently saturated or unsaturated hydrocarbon groups having from about 1- 24 carbon atoms; wherein R' is methyl or hydrogen; wherein n = 1-100; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base. In a preferred embodiment, R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 4-24 carbon atoms, R' is 20 methyl or hydrogen, R<sub>2</sub> is methyl, ethyl, or propyl, and mixtures thereof, M<sup>+</sup> is a conjugate

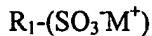
acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof, and n = 1-100. In another preferred embodiment, the surface active agent is of the formula:

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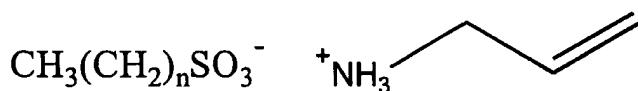


wherein n1 = 2 - 18; and wherein n2 = 1 - 20.

The present invention further encompasses surface active agents of the formula:



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6 - 24 carbon atoms and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base. In a preferred embodiment, R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms, and M<sup>+</sup> is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof. In another preferred embodiment, the surface active agent is of the formula:



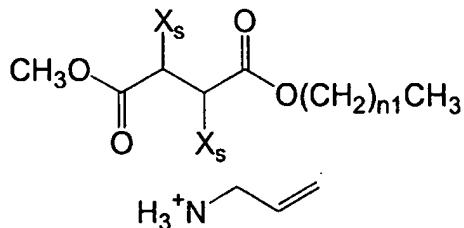
wherein n = 5 - 17.

The present invention further encompasses surface active agents of the formula:



wherein R<sub>1</sub> and R<sub>2</sub> are independently saturated or unsaturated hydrocarbon groups having from about 1- 24 carbon atoms; wherein n = 0-10; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base. In a preferred embodiment, R<sub>1</sub> and R<sub>2</sub> are independently saturated or

unsaturated hydrocarbon groups having from about 1 - 24 carbon atoms, n = 1-6, and M<sup>+</sup> is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof. In another preferred embodiment, the surface active agent is of the formula:

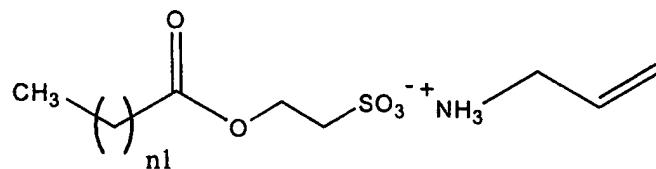


wherein n1 is zero or an integer of from 1-17; and X<sub>s</sub> represents SO<sub>3</sub><sup>-</sup>.

The present invention further encompasses surface active agents of the formula:



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein n = 1-10; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base. In a preferred embodiment, R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms, n = 1-5, and M<sup>+</sup> is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting essentially of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, or a mixture thereof. In another preferred embodiment, the surface active agent is of the formula:

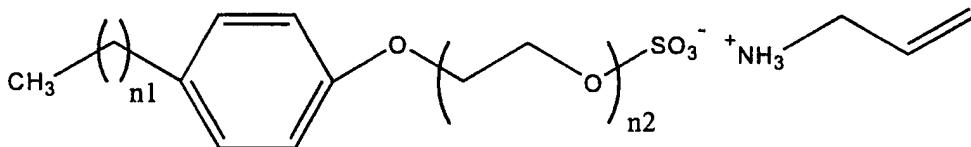


20                    wherein n1 = 2 -18.

The present invention further encompasses surface active agents of the formula:

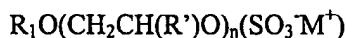


wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms; wherein Ar is a phenyl, polyphenyl, napthyl, polynapthyl, styryl, or polystyryl group, 5 and mixtures thereof; wherein  $R'$  is methyl or hydrogen; wherein  $M^+$  is a conjugate acid of the nitrogenous base; wherein  $n = 1-4$ ; wherein the total number of carbon atoms represented by  $(R_1)_n$  is at least 5; and wherein  $m = 0-100$ . In a preferred embodiment,  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms, Ar is phenyl;  $M^+$  is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group 10 consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof,  $n = 1$ , and  $m = 0-100$ . In another preferred embodiment, the surface active agent is of the formula:



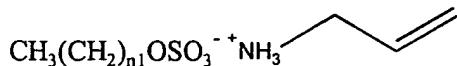
wherein  $n1 = 5 - 18$ ; and wherein  $n2 = 0 - 20$ .

15 The present invention further encompasses surface active agents of the formula:

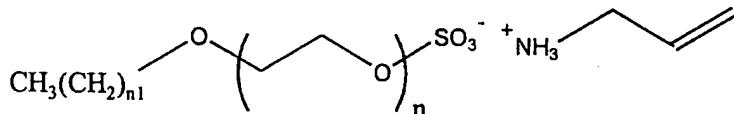


wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 1 - 24 carbon atoms; wherein  $R'$  is methyl or hydrogen; wherein  $n = 0-100$ ; and wherein  $M^+$  is a conjugate acid of the nitrogenous base. In a preferred embodiment,  $R_1$  is a saturated or unsaturated 20 hydrocarbon group having from about 6- 24 carbon atoms,  $R'$  is methyl or hydrogen,  $n = 0-100$ , and  $M^+$  is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl

N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof. In another preferred embodiment, the surface active agent is of the formula:



wherein  $n_1 = 5 - 18$ . In another preferred embodiment, the surface active agent is of the formula:

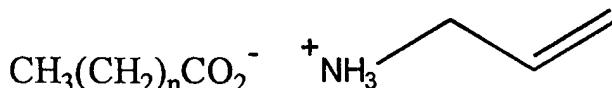


wherein  $n_1 = 5 - 18$ ; and wherein  $n = 1 - 20$ .

The present invention further encompasses surface active agents of the formula:



wherein  $\text{R}_1$  is a saturated or unsaturated hydrocarbon group having from about 4 - 24 carbon atoms; and wherein  $\text{M}^+$  is a conjugate acid of the nitrogenous base. In a preferred embodiment,  $\text{R}_1$  is a saturated or unsaturated hydrocarbon group having from about 6 - 24 carbon atoms, and  $\text{M}^+$  is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof. In another preferred embodiment, the surface active agent is of the formula:



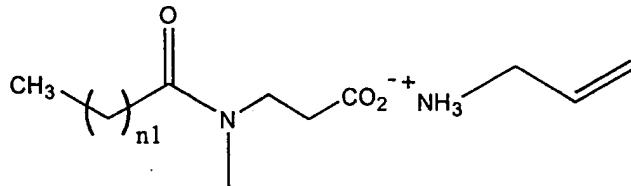
wherein  $n = 5 - 18$ .

The present invention further encompasses surface active agents of the formula:



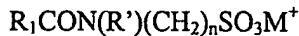
wherein  $\text{R}_1$  is a saturated or unsaturated hydrocarbon group having from about 1 - 24 carbon atoms; wherein  $\text{R}'$  is methyl, ethyl, propyl or hydrogen; wherein  $\text{M}^+$  is a conjugate acid of the

nitrogenous base; and wherein n = 1-10. In a preferred embodiment, M<sup>+</sup> is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof, R' is methyl, ethyl, propyl or hydrogen,  
5 and n = 2-5. In another preferred embodiment, the surface active agent is of the formula:

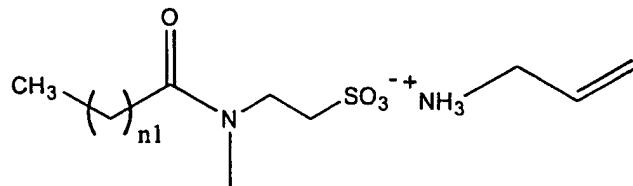


wherein  $n_1 = 2 - 18$ .

The present invention further encompasses surface active agents of the formula:

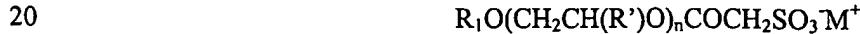


10 wherein  $\text{R}_1$  is a saturated or unsaturated hydrocarbon group having from about 1 - 24 carbon atoms; wherein R' is methyl, ethyl, propyl or hydrogen; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; and wherein n = 1-10. In a preferred embodiment, M<sup>+</sup> is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof, R' is methyl, ethyl, propyl or hydrogen,  
15 and n = 2-5. In another preferred embodiment, the surface active agent is of the formula:

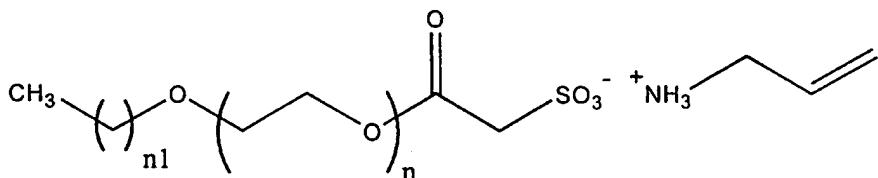


wherein  $n_1 = 2 - 18$ .

The present invention further encompasses surface active agents of the formula:

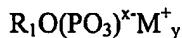


wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein R' is methyl or hydrogen; wherein n = 0-100; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base. In a preferred embodiment, R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms; R' is methyl or hydrogen, M<sup>+</sup> is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; and n = 0-100. In another preferred embodiment, the surface active agent is of the formula:



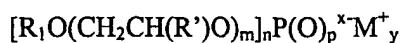
wherein n1 = 5 - 17; and wherein n = 0 - 20.

The present invention further encompasses surface active agents of the formula:



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms, phenyl, polyphenyl, napthyl, polynapthyl, styryl, or polystyryl group, an alkyl/alkoxylate substituted phenyl, an alkyl/alkoxylate substituted or poly-substituted polyphenyl, an alkyl/alkoxylate substituted or poly-substituted napthyl, an alkyl/alkoxylate substituted or poly-substituted polynapthyl, an alkyl/alkoxylate substituted or poly-substituted styryl, or an alkyl/alkoxylate substituted or poly-substituted polystyryl group, and mixtures thereof; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; wherein x = 1 or 2; and wherein y = 1 or 2.

The present invention further encompasses surface active agents of the formula:



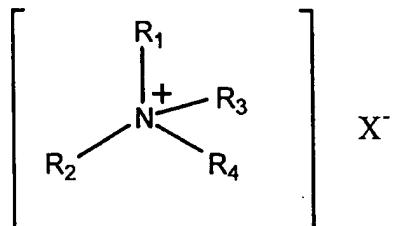
wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein R' is methyl or hydrogen; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; m = 0 -100; wherein n = 1 or 2; wherein p = 2 or 3; wherein x = 1 or 2; and wherein y = 1 or 2.

The present invention further encompasses surface active agents of the formula:



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein Ar is phenyl; wherein R' is methyl or hydrogen; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base, the nitrogenous base selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; wherein n = 1-4; wherein m = 0 -100; wherein q = 1 or 2; wherein p = 2 or 3; wherein x = 1 or 2; and wherein y = 1 or 2.

The present invention further encompasses polymerizable surface active agents which are ammonium salts of the general formula:



wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are independently, substituted or unsubstituted hydrocarbyl groups of from about 1 to about 30 carbon atoms, or hydrocarbyl groups having from about 1 to 20 about 30 carbon atoms and containing one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the R<sub>1</sub>-R<sub>4</sub> groups contains at least one or more ethenylene groups; and wherein X<sup>-</sup> is an anion

group selected from the group consisting of sulfonate, sulfate, sulfinate, sulfenate, phosphate, carboxylate, nitrate, and acetate. Polymerizable surface active agents of the present invention include those of the above general formula in the form of ring structures formed by covalently linking two of the R<sub>1</sub>-R<sub>4</sub> groups. Examples include unsaturated imidazolines, imidazoliniums, 5 and pyridiniums, and the like.

All of the documents, e.g., patents and journal articles, cited above or below are hereby incorporated by reference in their entirety.

In the following examples, all amounts are stated in percent by weight of active material unless indicated otherwise. One skilled in the art will recognize that modifications 10 may be made in the present invention without deviating from the spirit or scope of the invention. The invention is illustrated further by the following examples which are not to be construed as limiting the invention or scope of the specific procedures or compositions described herein. As used in the examples appearing below, the following designations, symbols, terms and abbreviations have the indicated meanings:

15

| <u>Material</u>  | <u>Definition</u>  |
|------------------|--|
| Polystep® A-13   | Linear dodecylbenzene sulfonic acid (commercially available from Stepan Company, Northfield Illinois)                |
| Polystep® A-16   | Branched dodecylbenzene sulfonic acid, sodium salt (commercially available from Stepan Company, Northfield Illinois) |
| Polystep® A-17   | Branched dodecylbenzene sulfonic acid (commercially available from Stepan Company, Northfield Illinois)              |
| Cedephos® CP-610 | Nonyl Phenol 9-EO Phosphoric Acid Ester (commercially available from Stepan Company, Northfield Illinois)            |

25

Procedures

Due to their amphiphilic character, surfactants have a tendency to adsorb at various liquid-liquid and liquid-air interfaces, which leads to a reduction of surface or interfacial tension. After saturating an interface, these surface active molecules begin to aggregate in the solution to form micelles at a specific surfactant concentration known as the critical micelle concentration (CMC). The adsorption characteristics and the micellization behavior of surfactants are responsible for the technologically important properties of surfactants, such as wetting, solubilization, emulsification, and the like. Thus, the efficiency of any surface active agent relates to its ability to lower interfacial tension, form micelles, and display favorable adsorption characteristics by providing efficient packing of the surface active molecules at the interface in a very small concentration.

The following test procedures were used to evaluate the ethylenically unsaturated amine salts of the present invention. A fully automated Kruss K-12 tensiometer was used to measure the adsorption and micellar behavior of the polymerizable, surface active agents. All of the measurements were done at room temperature, and distilled water was used for CMC measurements.

All <sup>1</sup>H NMR spectra were recorded using a 270 MHz Joel Delta NMR Fourier Transform Spectrometer. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) down field from tetramethylsilane (TMS) using internal TMS or residual non-deuterated solvent as a reference. Multiplicity is indicated by the following abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), heptet (h), multiplet (m), broad multiplet (br m) doublet of doublets (dd), etc. All samples were isolated in solid form by oven-drying in vacuo aqueous solution of the surface active agents to remove substantially all water from the sample; NMR data for all samples was acquired by dissolving the solid sample in CD<sub>3</sub>OD.

Example #1

Approximately 7.5 ml of allyl amine and about 150.0 g of deionized water were charged to a reaction vessel equipped with a means for agitation and a means for cooling. The allyl amine/water mixture temperature was adjusted to about 25°C and approximately 5 32.5 g of Polystep® A-13 was added, to give the desired ethylenically unsaturated amine salt as an approximately 20% active aqueous solution with a pH of about 6.5. The pH of the resulting salt solution may be adjusted as needed with the addition of more acid or amine; higher and lower pH materials may be produced as desired.  $^1\text{H}$  NMR:  $\delta$  7.8 (m, 2H), 7.2 (m, 2H), 6.0 (m, 1H), 5.4 (ddt, 2H), 5.0 (br, 3H), 3.6 (m, 2H), 1.7 (bm, 3H), 1.3 (bm, 16H), 0.9 10 (m, 6H). The CMC, Surface Tension Reduction, and Effectiveness of Surfactant are reported in Table I.

Example #2

Approximately 7.5 ml of allyl amine and about 150.0 g of deionized water were 15 charged to a reaction vessel equipped with a means for agitation and a means for cooling. The allyl amine/water mixture temperature was adjusted to about 25°C and approximately 32.5 g of Polystep® A-17 was added, to give the desired ethylenically unsaturated amine salt as an approximately 20% active aqueous solution with a pH of about 7.0. The pH of the resulting salt solution may be adjusted as needed with the addition of more acid or amine; 20 higher and lower pH materials may be produced as desired.  $^1\text{H}$  NMR:  $\delta$  7.8 (m, 2H), 7.4 (bt, 2H), 5.9 (ddt, 1H), 5.4 (m, 2H), 4.9 (br, 3H), 3.5 (dd, 2H), 2.9 (m, 1H), 1.6 (m, 3H), 0.9-1.1 (m, 28H).

Example #3

Approximately 12.3 ml of diallyl amine and about 170.0 g of deionized water were charged to a reaction vessel equipped with a means for agitation and a means for cooling. The diallyl amine/water mixture temperature was adjusted to about 25°C and approximately 5 32.5 g of Polystep® A-13 was added, to give the desired ethylenically unsaturated amine salt as an approximately 20% active aqueous solution with a pH of about 7.0. The pH of the resulting salt solution may be adjusted as needed with the addition of more acid or amine; higher and lower pH materials may be produced as desired.  $^1\text{H}$  NMR:  $\delta$  7.8 (m, 2H), 7.2 (m, 2H), 6.0 (m, 2H), 5.4 (m, 4H), 5.0 (br, 2H), 3.6 (m, 4H), 1.7 (bm, 4H), 1.3 (bm, 15H), 0.9 10 (bm, 6H).

Example #4

Approximately 12.3 ml of diallyl amine and about 170.0 g of deionized water were charged to a reaction vessel equipped with a means for agitation and a means for cooling. 15 The diallyl amine/water mixture temperature was adjusted to about 25°C and approximately 32.5 g of Polystep® A-17 was added, to give the desired ethylenically unsaturated amine salt as an approximately 20% active aqueous solution with a pH of about 7.0. The pH of the resulting salt solution may be adjusted as needed with the addition of more acid or amine; higher and lower pH materials may be produced as desired.  $^1\text{H}$  NMR:  $\delta$  7.8 (m, 2H), 7.5 (m, 2H), 5.9 (m, 2H), 5.4 (m, 4H), 4.9 (brs, 2H), 3.6 (m, 4H), 2.8 (m, 1H), 1.7 (bm, 3H), 0.9-1.1 20 (m, 28H).

Example #5 (Comparative Example)

Approximately 13.7 ml of propyl amine and about 170.0 g of deionized water were charged to a reaction vessel equipped with a means for agitation and a means for cooling. The propyl amine/water mixture temperature was adjusted to about 25°C and approximately 5 32.5 g of Polystep® A-13 was added, to give the saturated amine salt as an approximately 20% active aqueous solution with a pH of about 7.0. The pH of the resulting salt solution may be adjusted as needed with the addition of more acid or amine; higher and lower pH materials may be produced as desired.  $^1\text{H}$  NMR:  $\delta$  7.8 (dd, 2H), 7.23 (t, 2H), 4.9 (br, 2H), 2.85 (t, 2H), 1.6 (m, 6H), 1.2 (m, 14H), 0.9 (m, 6H). The CMC, Surface Tension Reduction, and 10 Effectiveness of the Surfactant are reported in Table I.

Example #6

Approximately 30.0 ml of allyl amine and about 408.0 g of deionized water were charged to a reaction vessel equipped with a means for agitation and a means for cooling. 15 The allyl amine/water mixture temperature was adjusted to about 25°C and approximately 80.0 g of lauric acid was added, to give the desired ethylenically unsaturated amine salt as an approximately 20% active aqueous solution with a pH of about 7.0. (The carboxylic acid may be a solid at room temperature and can be pre-melted prior to addition to the amine/water mixture, for ease of handling. As an alternative, the carboxylic acid and water may be 20 combined and heated to produce a uniform mixture, i.e., 50-60°C for lauric acid, followed by addition of the unsaturated amine.) The pH of the resulting salt solution may be adjusted as needed with the addition of more acid or amine; higher and lower pH materials may be produced as desired.  $^1\text{H}$  NMR:  $\delta$  6.0 (m, 1H), 5.5 (ddt, 2H), 3.6 (m, 2H), 2.3 (t, 2H), 1.6 (br, 2H), 1.42 (s, 5H, residual water), 1.41 (s, 3H), 1.4 (br, 18H), 0.9 (t, 3H).

Example #7 (Comparative Example)

Approximately 16.4 ml of propyl amine and about 210.0 g of deionized water were charged to a reaction vessel equipped with a means for agitation and a means for cooling. The propyl amine/water mixture temperature was adjusted to about 25°C and approximately 5 40.0 g of lauric acid was added, to give the saturated amine salt as an approximately 20% active aqueous solution with a pH of about 7.0. (The carboxylic acid may be a solid at room temperature and can be pre-melted prior to addition to the amine/water mixture, for ease of handling. As an alternative, the carboxylic acid and water may be combined and heated to produce a uniform mixture, i.e., 50-60°C for lauric acid, followed by addition of the saturated 10 amine.) The pH of the resulting salt solution may be adjusted as needed with the addition of more acid or amine; higher and lower pH materials may be produced as desired.  $^1\text{H}$  NMR:  $\delta$  5.0 (s, 3H), 3.3 (p, 2H), 2.8 (dt, 2H), 2.25 (t, 2H), 1.6 (m, 2H), 1.3 (m, 17H), 1.0 (t, 3H), 0.9 (t, 3H).

15

Example #8

Approximately 5.1 ml of allyl amine and about 320.0 g of deionized water were charged to a reaction vessel equipped with a means for agitation and a means for cooling. The allyl amine/water mixture temperature was adjusted to about 25°C and approximately 20 75.0 g of Cedephos CP-610 was added, to give the desired unsaturated amine salt as an approximately 20% active aqueous solution with a pH of about 7.0. (The phosphoric acid ester may be a solid at room temperature and can be pre-melted prior to addition to the amine/water mixture, for ease of handling. As an alternative, the phosphoric acid ester and water may be combined and heated to produce a uniform mixture, followed by addition of the unsaturated amine.) The pH of the resulting salt solution may be adjusted as needed with the 25 addition of more acid or amine; higher and lower pH materials may be produced as desired.

<sup>1</sup>H NMR: δ 7.2 (m, 2H), 6.8 (m, 2H), 6.0 (m, 1H), 5.4 (m, 2H), 4.1 (m, 2H), 3.8 (m, 2H), 3.6 (m, 32H), 0.4-1.8 (m, 19H). The CMC, Surface Tension Reduction, and Effectiveness of the Surfactant are reported in Table I.

5       Example #9 (Comparative Example)

Approximately 5.1 ml of propyl amine and about 320.0 g of deionized water were charged to a reaction vessel equipped with a means for agitation and a means for cooling. The propyl amine/water mixture temperature was adjusted to about 25°C and approximately 75.0 g of Cedephos CP-610 was added, to give the desired saturated amine salt as an 10 approximately 20% active aqueous solution with a pH of about 7.0. (The phosphoric acid ester may be a solid at room temperature and can be pre-melted prior to addition to the amine/water mixture, for ease of handling. As an alternative, the phosphoric acid ester and water may be combined and heated to produce a uniform mixture, followed by addition of the unsaturated amine.) The pH of the resulting salt solution may be adjusted as needed with the 15 addition of more acid or amine; higher and lower pH materials may be produced as desired.

<sup>1</sup>H NMR: δ 7.2 (m, 2H), 6.8 (m, 2H), 4.9 (s, 3H), 4.1 (m, 2H), 3.8 (m, 2H), 3.6 (m, 32H), 3.3 (t, 2H), 2.9 (dt, 2H), 0.4-1.8 (m, 22H). The CMC, Surface Tension Reduction, and Effectiveness of the Surfactant are reported in Table I.

20

Table I: Surface Tension Data for Ethylenically Unsaturated Amine Salts of Sulfonic Acids, Carboxylic Acids and Phosphoric Acid Esters, Including Comparative Examples

| Example # | Ethylenically Unsaturated Amine Salt            | CMC (mg/l) | Surface Tension at CMC (mN/m) | Effectiveness of Surface Tension Reduction at CMC (mN/m) |
|-----------|---|------------|-------------------------------|--|
| 1         | Allylamine Salt of Dodecylbenzene Sulfonic Acid | 100.5      | 33.2                          | 39.1   |
| 5*        | Propylamine Salt of Dodecylbenzene Sulfonic     | 480.5      | 31.0                          | 41.3   |

|                | Acid   |       |      |      |
|----------------|--|-------|------|------|
| Polystep® A-16 | Sodium Salt of Dodecylbenzene Sulfonic Acid                | 156.0 | 35.0 | 37.3 |
| 8              | Allylamine Salt of Nonylphenol 9-EO Phosphoric Acid Ester  | 31.8  | 30.0 | 42.3 |
| 9*             | Propylamine Salt of Nonylphenol 9-EO Phosphoric Acid Ester | 74    | 31.5 | 40.8 |

\* comparative example

Example #10: Emulsion Polymerization With Polystep A-17 Allyl Amine Salt

An emulsion polymerization kettle equipped with a nitrogen inlet, a heating means, and an agitation means, is charged with 250 g of water and 8.13 g of Polystep A-17 allyl amine salt. The mixture is heated to approximately 85 °C. Approximately 17 g of a 4% aqueous ammonium persulfate solution (i.e. initiator solution) is added and approximately 75 g of monomer solution is added while mixing, the monomer solution comprising 48 % butyl acrylate, 49 % methyl methacrylate and 3 % methacrylic acid. After mixing for 15 minutes, 298 g of monomer solution is added over 2.5 hours. After monomer solution addition has commenced for 30 minutes, 67 g of initiator solution (described above) and 75 g of Polystep A-17 allyl amine salt in 35 g of water, are added separately and concurrently, over 2 hours. The resulting mixture is agitated at 85 °C for another hour cooled, pH adjusted with dilute NhyOH, followed by discharging the reactor to give an all acrylic latex with the following properties: Viscosity: 50 centipoise; pH: 6.4; Solids: 45.6(actual), 46.7(theoretical); Particle Size: 115.

Example 11

A methylmethacrylate/butylacrylate/methacrylic acid (MMA/BA/MMA) co-polymer (in a weight ratio of about 48:49:3), in combination with the allylamine salt of laureth-3EO-

sulfate (AES-3), is prepared as follows. About 205 g of deionized water and about 1.6 g of AAES-3 (as a 25.5% active aqueous solution), are placed in a reactor suitable for emulsion polymerization, equipped with agitation means, heating means and cooling means. With agitation, the reactor is purged with nitrogen (99% pure), and heated to about 77 - 79°C.

5 Next, about 75 g of the monomer mixture (20% of a total of 376 g of the MMA/BA/MMA monomer mixture in the ratio above) is added to the reactor. After 10 minutes, 15.0 g of a solution of ammonium persulfate (20% of the total solution of 1.9 g of ammonium persulfate dissolved in 72.9 g of water) is added to the reactor over a period of about 4 minutes with continued agitation, during which time there is an exotherm of about 12-14°C. After the

10 exotherm is complete, about 301 g of the monomer mixture (the remaining 80% MMA/BA/MMA monomer mixture), 59.8 g of the ammonium persulfate solution (the remaining 80 %) , and 22.0 g of AAES-3 (as the 22% active aqueous solution) are charged to the reactor over a period of 2 hours with continued agitation, while keeping the reactor contents at a temperature of about 78 - 82°C. The reactor temperature is then elevated to

15 about 82 - 84°C with continued agitation, for about 15 minutes. After this 15 minute period, the reactor is cooled to about 30°C. The resulting latex product is completely removed from the reactor and gravity filtered using a first 420 mesh screen and then a second 250 mesh screen. The total latex coagulum (i.e. solids) from both mesh screens is collected, combined and weighed. The resulting latex has the following characteristics:

|                                  |                               |
|----------------------------------|-------------------------------|
| Solids (weight %)                | 50.36                         |
| Particle size (nm)<br>Vol(50%)   | 95                            |
| PH                               | 2.50                          |
| Viscosity (3/60)<br>(centipoise) | 120.00                        |
| Coagulum                         | 0.26g (<0.04% on total batch) |

|  |        |
|--|--------|
|  | weight |
|--|--------|

Example 12

5 A methylmethacrylate/butylacrylate/methacrylic acid (MMA/BA/MMA) co-polymer  
(in a weight ratio of about 48:49:3), in combination with the allylamine salt of lauryl sulfate  
(AS), is prepared as follows. About 222 g of deionized water and about 2.3 g of AS (as a  
17.2% active aqueous solution), are placed in a reactor suitable for emulsion polymerization,  
equipped with agitation means, heating means and cooling means. With agitation, the reactor  
10 is purged with nitrogen (99% pure), and heated to about 77 - 79°C. Next, about 77 g of the  
monomer mixture (20% of a total of 378 g of the MMA/BA/MMA monomer mixture in the  
ratio above) is added to the reactor. After 10 minutes, 15.4 g of a solution of ammonium  
persulfate (20% of the total solution of 1.9 g of ammonium persulfate dissolved in 75.0 g of  
water) is added to the reactor over a period of about 4 minutes with continued agitation,  
15 during which time there is an exotherm of about 7-8°C. After the exotherm is complete,  
about 301 g of the monomer mixture (the remaining 80% MMA/BA/MMA monomer  
mixture), 61.6 g of the ammonium persulfate solution (the remaining 80 %) , and 33.7 g of  
AS (as the 17.2% active aqueous solution) are charged to the reactor over a period of 2 hours  
with continued agitation, while keeping the reactor contents at a temperature of about 78 -  
20 82°C. The reactor temperature is then elevated to about 82 - 84°C with continued agitation,  
for about 15 minutes. After this 15 minute period, the reactor is cooled to about 30°C. The  
resulting latex product is completely removed from the reactor and gravity filtered using a  
first 420 mesh screen and then a second 250 mesh screen. The total latex coagulum (i.e.  
solids) from both mesh screens is collected, combined and weighed. The resulting latex has  
25 the following characteristics:

|                    |       |
|--------------------|-------|
| Solids (weight %)  | 48.41 |
| Particle size (nm) | 95    |

|                                  |                                      |
|----------------------------------|--------------------------------------|
| Vol(50%)                         |                                      |
| PH                               | 2.43                                 |
| Viscosity (3/60)<br>(centipoise) | 140.00                               |
| Coagulum                         | 0.36g (<0,04% on total batch weight) |

From the foregoing, it will be appreciated that although specific embodiments of the invention have been described herein for purposes of illustration, various embodiments may  
5 be made without deviating from the spirit or scope of the invention.

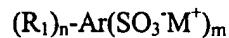
What is claimed is:

1. A polymerizable surface active agent comprising:
  - a) at least one acid, wherein the acid is a sulfonic acid, a sulfuric acid ester, a carboxylic acid, or a phosphoric acid, or a mixture thereof; and
  - b) at least one nitrogenous base, wherein the nitrogenous base contains at least one nitrogen atom and at least one ethylenically unsaturated moiety;  
wherein the polymerizable surface active agent is an amine salt.
2. A polymerizable surface active agent according to claim 1, comprising:
  - a) at least one acid, wherein the sulfonic acid is an  $\alpha$ -sulfonated alkyl ester acid, an  $\alpha$ -sulfonated ester diacid, or a mixture thereof, and the sulfuric acid ester is an alkoxylation alkyl sulfonic acid ester, an alkoxylation alkyl aryl surfuric acid ester, or a mixture thereof; and
  - b) at least one nitrogenous base, wherein the nitrogenous base contains at least one nitrogen atom and at least one ethylenically unsaturated moiety;  
wherein the polymerizable surface active agent is an amine salt.
3. A polymerizable, surface active agent according to claim 2, wherein the sulfonic acid is a polysulfonic acid, a sulfonic acid of an oil, a paraffin sulfonic acid, a lignin sulfonic acid, a petroleum sulfonic acid, an olefin sulfonic acid, a polyolefin sulfonic acid, a polyolefin polysulfonic acid or a mixture thereof, the carboxylic acid is a polycarboxylic acid, and the phosphoric acid is a polyphosphoric acid, a phosphinic acid, or a polyphosphinic acid, or a mixture thereof.
4. A polymerizable, surface active agent according to claim 2, wherein the nitrogenous base is allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-

allyl amine, N-allyl-N,N-dimethyl amine, methyl 3-amino crotonate, 3-amino crotononitrile, 3-amino-1-propanol vinyl ether, 2-(dimethylamino)ethyl acrylate, or 1,4-diamino-2-butene or a mixture thereof.

5        5. A polymerizable, surface active agent according to claim 4, wherein the nitrogenous base is allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine or 2-(dimethylamino)ethyl acrylate, or a mixture thereof.

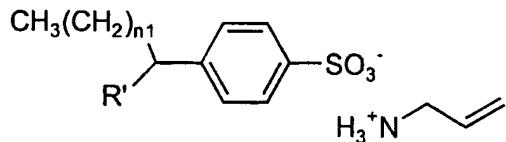
10      6. A polymerizable, surface active agent according to claim 2, which is of the formula:



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1-24 carbon atoms; wherein Ar is a phenyl, polyphenyl, napthyl, polynapthyl, styryl, or polystyryl group, or a mixture thereof; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; wherein n represents an integer of from 1-5 and m represents an integer of from 1-8; and wherein the total number of carbon atoms represented by (R<sub>1</sub>)<sub>n</sub> is at least 5.

20      7. A polymerizable, surface active agent according to claim 6, wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms; wherein Ar is phenyl; wherein the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; and wherein n is 1 and m is 1.

25      8. A polymerizable, surface active agent according to claim 7, which is of the formula:



wherein n1 represents an integer of from 4 -18; and wherein R' is hydrogen or saturated or unsaturated hydrocarbon group having from about 1-8 carbon atoms.

5 9. A polymerizable, surface active agent according to claim 2, which is of the  
formula:

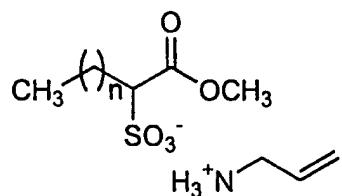


wherein R<sub>1</sub> and R<sub>2</sub> are independently saturated or unsaturated hydrocarbon groups having from about 1-24 carbon atoms; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base.

10

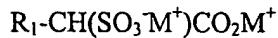
10. A polymerizable, surface active agent according to claim 9, wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms; wherein R<sub>2</sub> is methyl, ethyl, or propyl, or a mixture thereof; and wherein the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-15 methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof.

11. A polymerizable, surface active agent according to claim 10, which is of the formula:



20 wherein n represents an integer of from 3 - 18.

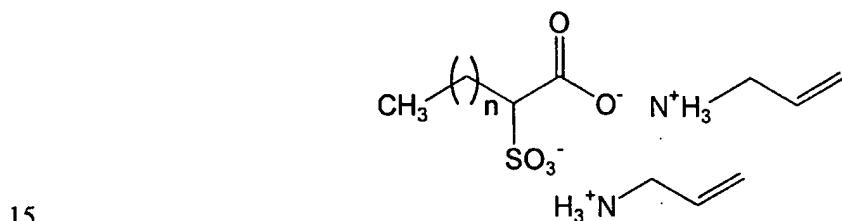
12. A polymerizable, surface active agent according to claim 2, which is of the formula:



wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 3 - 24 carbon atoms; and wherein  $M^+$  is a conjugate acid of the nitrogenous base.

13. A polymerizable, surface active agent according to claim 11, wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms; and wherein the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof.

14. A polymerizable, surface active agent according to claim 13, which is of the formula:



wherein n represents an integer of from 3 - 18.

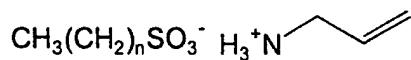
15. A polymerizable surface active agent according to claim 2, which is of the formula:



wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 6 - 24 carbon atoms; and wherein  $M^+$  is a conjugate acid of the nitrogenous base.

16. A polymerizable, surface active agent according to claim 15, wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms; and wherein the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof.

17. A polymerizable, surface active agent according to claim 16, which is of the formula:



10 wherein n represents an integer of from 5 - 17.

18. A polymerizable, surface active agent according to claim 2, which is of the formula:



15 wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1-24 carbon atoms; wherein Ar is a phenyl, polyphenyl, napthyl, polynapthyl, styryl, or polystyryl group, and mixtures thereof; wherein R' is methyl or hydrogen; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; wherein n represents an integer of from 1-4; wherein the total number of carbon atoms represented by (R<sub>1</sub>)<sub>n</sub> is at least 5; and wherein m is zero or an integer of from 1-20 100.

19. A polymerizable, surface active agent according to claim 18, wherein, R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms; wherein Ar is phenyl; wherein the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-

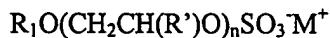
(dimethylamino)ethyl acrylate, and mixtures thereof; wherein n is 1; and wherein m is zero or an integer of from 1-100.

20. A polymerizable, surface active agent according to claim 19, which is of the  
5 formula:



wherein n1 represents an integer of from 5 -18; and wherein n2 represents an integer of from 0 - 20.

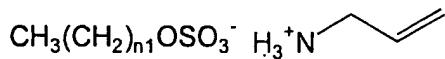
- 10 21. A polymerizable, surface active agent according to claim 2, which is of the  
formula:



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1 - 24 carbon atoms; wherein R' is methyl or hydrogen; wherein n is zero or an integer of from 1-100; and  
15 wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base.

22. A polymerizable, surface active agent according to claim 21, wherein R<sub>1</sub> is a  
saturated or unsaturated hydrocarbon group having from about 6- 24 carbon atoms; wherein  
R' is methyl or hydrogen; wherein n is zero or an integer of from 1-100; and wherein the  
20 nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl  
amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and  
mixtures thereof.

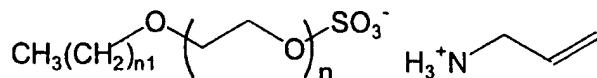
23. A polymerizable, surface active agent according to claim 22, which is of the formula:



wherein n1 represents an integer of from 5 - 18.

5

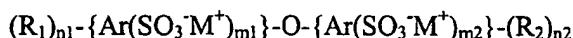
24. A polymerizable, surface active agent according to claim 23, which is of the formula:



wherein n1 represents an integer of from 5 - 18; and wherein n represents an integer of from 1

10 - 20.

25. A polymerizable, surface active agent according to claim 2, which is of the formula:



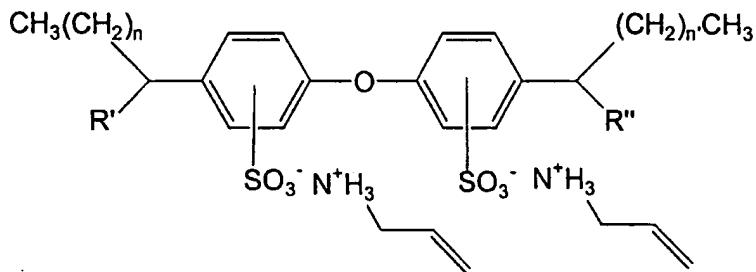
15 wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, or saturated or unsaturated hydrocarbon groups having from about 1-24 carbon atoms; wherein Ar is a phenyl, polyphenyl, napthyl, polynaphthyl, styryl, or polystyryl group, or a mixture thereof; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; wherein n1 and n2 are independently 0 - 5, provided that n1 and n2 are not both equal to zero; and wherein m1 and m2 are independently 0-8, provided that m1  
20 and m2 are not both equal to zero.

26. A polymerizable, surface active agent according to claim 25, wherein R<sub>1</sub> is hydrogen and R<sub>2</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms; wherein Ar is phenyl; wherein the nitrogenous base is selected from the group

consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; wherein n1 is 4 and n2 is 1; and wherein m1 and m2 both equal one.

5        27. A polymerizable, surface active agent according to claim 25, wherein R<sub>1</sub> and R<sub>2</sub> are independently saturated or unsaturated hydrocarbon groups having from about 6-24 carbon atoms; wherein Ar is phenyl, wherein the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; wherein n1 and n2 both 10 equal one; and wherein m1 and m2 both equal one.

28. A polymerizable, surface active agent according to claim 27, which is of the formula:



15        wherein n and n' are independently 4-18; and wherein R' and R'' are independently hydrogen, methyl, ethyl or propyl.

29. A polymerizable, surface active agent according to claim 2, which is of the formula:

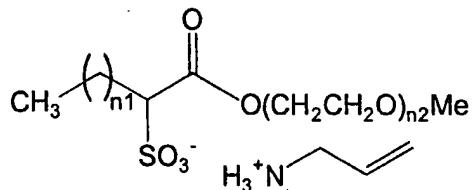


wherein R<sub>1</sub> and R<sub>2</sub> are independently saturated or unsaturated hydrocarbon groups having from about 1- 24 carbon atoms; wherein R' is methyl or hydrogen; wherein n represents an integer of from 1-100; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base.

5        30. A polymerizable, surface active agent according to claim 29, wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 4-24 carbon atoms; R' is methyl or hydrogen; R<sub>2</sub> is methyl, ethyl, or propyl, and mixtures thereof; the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof;

10      and wherein n represents an integer of from 1-100.

31. A polymerizable, surface active agent according to claim 30, which is of the formula:



15      wherein n1 represents an integer of from 2 - 18; and wherein n2 represents an integer of from 1 -20.

32. A polymerizable, surface active agent according to claim 2, which is of the formula:

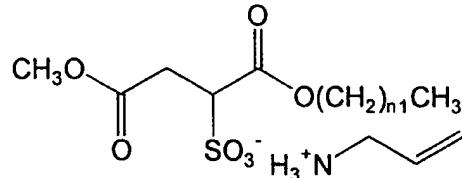


wherein R<sub>1</sub> and R<sub>2</sub> are independently saturated or unsaturated hydrocarbon groups having from about 1- 24 carbon atoms; wherein n is zero or an integer of from 1 - 10; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base.

33. A polymerizable, surface active agent according to claim 32, wherein R<sub>1</sub> and R<sub>2</sub> are independently saturated or unsaturated hydrocarbon groups having from about 1 - 24 carbon atoms; wherein n represents an integer of from 1-6; and wherein the nitrogenous base 5 is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof.

34. A polymerizable, surface active agent according to claim 33, which is of the formula:

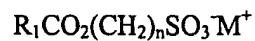
10



wherein n1 is zero or an integer of from 1- 17.

35. A polymerizable, surface active agent according to claim 2, which is of the formula:

15



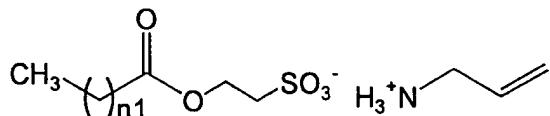
wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein n represents an integer of from 1-10; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base.

20

36. A polymerizable, surface active agent according to claim 35, wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms; wherein n is an integer of from 1-5; and wherein the nitrogenous base is selected from the group

consisting essentially of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, or a mixture thereof.

37. A polymerizable, surface active agent according to claim 36, which is of the  
5 formula:



wherein n1 is an integer of from 2 - 18.

38. A polymerizable, surface active agent according to claim 1, which is of the  
10 formula:

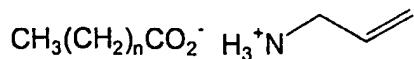


wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 4 - 24 carbon atoms; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base.

15 39. A polymerizable, surface active agent according to claim 38, wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6 - 24 carbon atoms; and wherein the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof.

20

40. A polymerizable, surface active agent according to claim 39, which is of the formula:



wherein n is an integer of from 5 - 18.

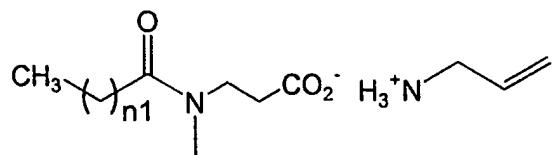
41. A polymerizable, surface active agent according to claim 1, which is of the formula:



5 wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 1 - 24 carbon atoms; wherein  $R'$  is methyl, ethyl, propyl or hydrogen; wherein  $M^+$  is a conjugate acid of the nitrogenous base; and wherein  $n$  is an integer of from 1-10.

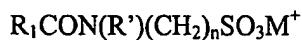
42. A polymerizable, surface active agent according to claim 41, wherein the  
10 nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; wherein  $R'$  is methyl, ethyl, propyl or hydrogen; and wherein  $n$  is an integer of from 2-5.

15 43. A polymerizable, surface active agent according to claim 42, which is of the formula:



wherein  $n1$  is an integer of from 2 - 18.

20 44. A polymerizable, surface active agent according to claim 2, which is of the formula:

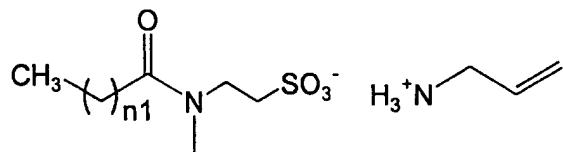


wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1 - 24 carbon atoms; wherein R' is methyl, ethyl, propyl or hydrogen; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; and wherein n is an integer of from 1-10.

5        45. A polymerizable, surface active agent according to claim 44, wherein the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; wherein R' is methyl, ethyl, propyl or hydrogen; and wherein n is an integer of from 2-5.

10

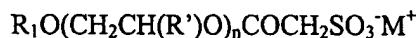
46. A polymerizable, surface active agent according to claim 45, which is of the formula:



wherein n1 is an integer of from 2 - 18.

15

47. A polymerizable, surface active agent according to claim 2, which is of the formula:



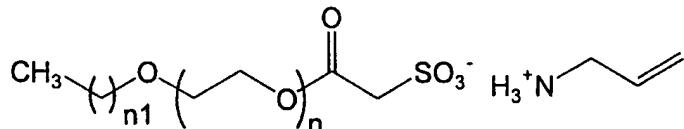
wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein R' is methyl or hydrogen; wherein n is zero or an integer of from 1-100; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base.

48. A polymerizable, surface active agent according to claim 47, wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 6-24 carbon atoms; wherein R' is methyl or hydrogen; wherein the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; and wherein n is zero or an integer of from 1-100.

5

49. A polymerizable, surface active agent according to claim 48, which is of the formula:

10



wherein n1 is an integer of from 5 - 17; and wherein n is zero or an integer of from 1 - 20.

50. A polymerizable, surface active agent according to claim 1, which is of the formula:

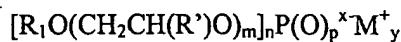
15



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms, phenyl, polyphenyl, napthyl, polynapthyl, styryl, or polystyryl group, an alkyl/alkoxylate substituted phenyl, an alkyl/alkoxylate substituted or poly-substituted polyphenyl, an alkyl/alkoxylate substituted or poly-substituted napthyl, an alkyl/alkoxylate substituted or poly-substituted polynapthyl, an alkyl/alkoxylate substituted or poly-substituted styryl, or an alkyl/alkoxylate substituted or poly-substituted polystyryl group, and mixtures thereof; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; wherein x is 1 or 2; and y is 1 or 2.

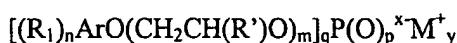
20

51. A polymerizable, surface active agent according to claim 1, which is of the formula:



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein R' is methyl or hydrogen; wherein the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; m is zero or an integer of from 1 -100; n is 1 or 2; p is 2 or 3; x is 1 or 2; and y is 1 or 2.

10 52. A polymerizable, surface active agent according to claim 1, which is of the formula:



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein Ar is phenyl; wherein R' is methyl or hydrogen; wherein the nitrogenous base is selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; wherein n is an integer of from 1-4; wherein m is zero or an integer of from 1 -100; wherein q is 1 or 2; wherein p is 2 or 3; wherein x is 1 or 2; and wherein y is 1 or 2.

20 53. An aqueous, surface active solution, comprising:

a) a polymerizable surface active agent comprising:

i) at least one acid, wherein the acid is a sulfonic acid, a sulfuric acid ester, a carboxylic acid, or a phosphoric acid, or a mixture thereof; and

- iii) at least one nitrogenous base, wherein the nitrogenous base contains at least one nitrogen atom and at least one ethylenically unsaturated moiety;

wherein the polymerizable surface active agent is an amine salt; and

- 5 b) water.

54. An aqueous, surface active solution according to claim 53, comprising:

a) a polymerizable surface active agent comprising:

1. at least one acid, wherein the acid is a sulfonic acid, a sulfuric acid ester, an alkoxylated alkyl sulfuric acid ester, an  $\alpha$ -sulfonated alkyl ester acid, an  $\alpha$ -sulfonated ester diacid, an alkoxylated alkyl aryl surfuric acid esters or a mixture thereof; and
2. at least one nitrogenous base, wherein the nitrogenous base contains at least one nitrogen atom and at least one ethylenically unsaturated moiety;

15 wherein the polymerizable, surface active agent is an amine salt; and

- b) water.

55. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:

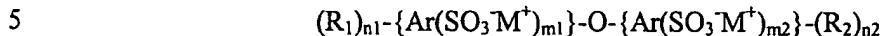


wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 1-24 carbon atoms; wherein Ar is a phenyl, polyphenyl, napthyl, polynapthyl, styryl, or polystyryl group, or a mixture thereof; wherein  $M^+$  is a conjugate acid of the nitrogenous base; wherein n is an integer of from 1-5 and m is an integer of from 1-8; and wherein the total number of carbon atoms represented by  $(R_1)_n$  is at least 5; and

b) water.

56. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:



wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen, or saturated or unsaturated hydrocarbon groups having from about 1-24 carbon atoms; wherein Ar is a phenyl, polyphenyl, naphthyl, polynaphthyl, styryl, or polystyryl group, or a mixture thereof; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; wherein n1 and n2 are independently 0 - 5, provided that n1 and n2  
10 are not both equal to zero; and wherein m1 and m2 are independently 0-8, provided that m1 and m2 are not both equal to zero; and

b) water.

57. An aqueous, surface active solution, according to claim 53, comprising:

15                   a) a polymerizable, surface active agent of the formula:

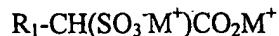


wherein R<sub>1</sub> and R<sub>2</sub> are independently saturated or unsaturated hydrocarbon groups having from about 1- 24 carbon atoms; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base.; and

20                   b) water.

58. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 3 - 24 carbon  
25 atoms; and wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; and

b) water.

59. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:



wherein  $R_1$  and  $R_2$  are independently saturated or unsaturated hydrocarbon groups having from about 1- 24 carbon atoms; wherein  $R'$  is methyl or hydrogen; wherein  $n$  is an integer of from 1-100; and wherein  $M^+$  is a conjugate acid of the nitrogenous base; and

b) water.

10

60. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:



wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 6 - 24 carbon atoms; and wherein  $M^+$  is a conjugate acid of the nitrogenous base; and

b) water.

61. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:



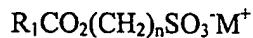
wherein  $R_1$  and  $R_2$  are independently saturated or unsaturated hydrocarbon groups having from about 1- 24 carbon atoms; wherein  $n$  is zero or an integer of from 1 - 10; and wherein  $M^+$  is a conjugate acid of the nitrogenous base; and

b) water.

25

62. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:



wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein n is an integer of from 1-10; and wherein  $M^+$  is a conjugate acid of the nitrogenous base; and

b) water.

63. An aqueous, surface active solution, according to claim 53, comprising:

10 a) a polymerizable, surface active agent of the formula:



wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 1-24 carbon atoms; wherein Ar is a phenyl, polyphenyl, napthyl, polynapthyl, styryl, or polystyryl group, and mixtures thereof; wherein  $R'$  is methyl or hydrogen; wherein  $M^+$  is a conjugate acid of the nitrogenous base; wherein n is an integer of from 1-4; wherein the total number of carbon atoms represented by  $(R_1)_n$  is at least 5; and wherein m zero or an integer of from 1-100; and

15 b) water.

64. An aqueous, surface active solution, according to claim 53, comprising:

20 a) a polymerizable, surface active agent of the formula:

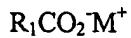


wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 1 - 24 carbon atoms; wherein  $R'$  is methyl or hydrogen; wherein n is zero or an integer of from 1-100; and wherein  $M^+$  is a conjugate acid of the nitrogenous base; and

25 b) water.

65. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:



5 wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 4 - 24 carbon atoms; and wherein  $M^+$  is a conjugate acid of the nitrogenous base; and

b) water.

66. An aqueous, surface active solution, according to claim 53, comprising:

10 a) a polymerizable, surface active agent of the formula:

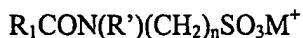


wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 1 - 24 carbon atoms; wherein  $R'$  is methyl, ethyl, propyl or hydrogen; wherein  $M^+$  is a conjugate acid of the nitrogenous base; and wherein  $n$  is an integer of from 1-10; and

15 b) water.

67. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:

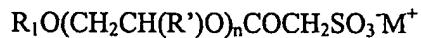


20 wherein  $R_1$  is a saturated or unsaturated hydrocarbon group having from about 1 - 24 carbon atoms; wherein  $R'$  is methyl, ethyl, propyl or hydrogen; wherein  $M^+$  is a conjugate acid of the nitrogenous base; and wherein  $n$  is an integer of from 1-10; and

b) water.

25 68. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein R' is methyl or hydrogen; wherein n is zero or an integer of from 1-100;

5 wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; and

b) water.

69. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:

10



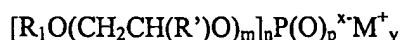
wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms, phenyl, polyphenyl, naphthyl, polynaphthyl, styryl, or polystyryl group, an alkyl/alkoxylate substituted phenyl, an alkyl/alkoxylate substituted or poly-substituted

15 polyphenyl, an alkyl/alkoxylate substituted or poly-substituted naphthyl, an alkyl/alkoxylate substituted or poly-substituted polynaphthyl, an alkyl/alkoxylate substituted or poly-substituted styryl, or an alkyl/alkoxylate substituted or poly-substituted polystyryl group, and mixtures thereof; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base; wherein x is 1 or 2; and wherein y is 1 or 2; and

20 b) water.

70. An aqueous, surface active solution, according to claim 53, comprising:

a) a polymerizable, surface active agent of the formula:



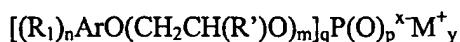
wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein R' is methyl or hydrogen; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base, selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof;

5       wherein m is zero or an integer of from 1 -100; wherein n is 1 or 2; wherein p is 2 or 3; wherein x is 1 or 2; and wherein y is 1 or 2; and

b) water.

71. An aqueous, surface active solution, according to claim 53, comprising:

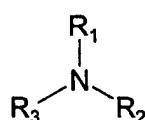
10      a) a polymerizable, surface active agent of the formula:



wherein R<sub>1</sub> is a saturated or unsaturated hydrocarbon group having from about 1- 24 carbon atoms; wherein Ar is phenyl; wherein R' is methyl or hydrogen; wherein M<sup>+</sup> is a conjugate acid of the nitrogenous base, selected from the group consisting of allyl amine, diallyl amine, triallyl amine, methallyl amine, N-methyl N-allyl amine, or 2-(dimethylamino)ethyl acrylate, and mixtures thereof; wherein n is an integer of from 1-4; wherein m is zero or an integer of from 1 -100; wherein q is 1 or 2; wherein p is 2 or 3; wherein x is 1 or 2; and wherein y is 1 or 2; and wherein the number of carbon atoms represented by (R<sub>1</sub>)<sub>n</sub> is at least about 5 when m is 0 and q is 1; and

20      b) water.

72. A polymerizable, surface active agent according to claim 1, wherein the nitrogenous base is a compound of the formula:



wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are independently hydrogen or organic groups containing an ethenylene group, provided that at least one of the R<sub>1</sub>-R<sub>3</sub> groups is a straight or branched chain alkylo group containing 1-8 carbon atoms and an ethenylene functionality.

# INTERNATIONAL SEARCH REPORT

|                              |
|------------------------------|
| International Application No |
| PCT/US 98/01065              |

|   |  |  |  |  |                       |
|---|--|--|--|--|-----------------------|
| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>IPC 6 C07C53/126 C07C233/47 C07C305/10 C07C309/04 C07C309/10<br>C07C309/15 C07C309/17 C07C309/31 C07C309/42 C07F9/09<br>C11D1/04 C11D1/12 C11D1/34  |  |  |  |  |                       |
| According to International Patent Classification(IPC) or to both national classification and IPC  |  |  |  |  |                       |
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>IPC 6 C07C C11D   |  |  |  |  |                       |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched   |  |  |  |  |                       |
| Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  |  |  |  |  |                       |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>   |  |  |  |  |                       |
| Category  | Citation of document, with indication, where appropriate, of the relevant passages                                 |  |  |  | Relevant to claim No. |
| A   | DE 34 26 197 A (AGFA GEVAERT) 23 January 1986<br>see page 16 - page 22; claims 1,7<br>---                          |  |  |  | 1                     |
| A   | US 5 478 883 A (M.J. ANCHOR, ET AL.) 26 December 1995<br>cited in the application<br>see the whole document<br>--- |  |  |  | 1                     |
| A   | US 5 162 475 A (R.H. TANG, ET AL.) 10 November 1992<br>cited in the application<br>see the whole document<br>---   |  |  |  | 1                     |
| A   | US 4 337 185 A (R.A. WESSLING, ET AL.) 29 June 1982<br>cited in the application<br>see the whole document<br>---   |  |  |  | 1                     |
|   |  |  |  |  | -/-                   |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.  |  |  | <input checked="" type="checkbox"/> Patent family members are listed in annex. |  |                       |
| * Special categories of cited documents :<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier document but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed  |  |  |  |  |                       |
| "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone<br>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<br>"&" document member of the same patent family |  |  |  |  |                       |
| Date of the actual completion of the international search   |  |  | Date of mailing of the international search report                             |  |                       |
| 27 May 1998   |  |  | 04/06/1998   |  |                       |
| Name and mailing address of the ISA<br>European Patent Office, P.O. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016  |  |  | Authorized officer<br><br>English, R   |  |                       |

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**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category | Citation of document, with indication, where appropriate, of the relevant passages                            | Relevant to claim No. |
|----------|---|-----------------------|
| A        | US 4 049 608 A (R. STECKLER, ET AL.) 20<br>September 1977<br>cited in the application<br>see claim 1<br>----- | 1                     |

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/US 98/01065

| Patent document cited in search report | Publication date | Patent family member(s)   |  | Publication date   |
|--|------------------|---|--|--|
| DE 3426197 A                           | 23-01-1986       | DE 3562368 A<br>EP 0168749 A<br>JP 61087649 A   |  | 01-06-1988<br>22-01-1986<br>06-05-1986   |
| US 5478883 A                           | 26-12-1995       | AU 5054396 A<br>CA 2173814 A<br>EP 0737693 A<br>JP 8337608 A  |  | 24-10-1996<br>12-10-1996<br>16-10-1996<br>24-12-1996   |
| US 5162475 A                           | 10-11-1992       | US 5296627 A<br>AU 621916 B<br>AU 3877989 A<br>EP 0422120 A<br>JP 2672385 B<br>JP 3503168 T<br>WO 8912618 A |  | 22-03-1994<br>26-03-1992<br>12-01-1990<br>17-04-1991<br>05-11-1997<br>18-07-1991<br>28-12-1989 |
| US 4337185 A                           | 29-06-1982       | AU 556895 B<br>AU 8540382 A<br>JP 59008702 A<br>US 4427819 A  |  | 27-11-1986<br>05-01-1984<br>18-01-1984<br>24-01-1984   |
| US 4049608 A                           | 20-09-1977       | NONE  |  |  |